IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Yoshitaka HAMADA et al. Art Unit: 2813
Serial No.: 10/796,656 Examiner: Stephen W. Smoot
Filing Date: March 9, 2004
For: Composition For Forming Porous Film and Method For Forming The Same, Porous Film and Method For Forming The Same, Interlevel Insulator Film, and Semiconductor Device

Assistant Commissioner for Patents
Washington, D. C. 20231

DECLARATION PURSUANT TO RULE 132

I, Yoshitaka HAMADA, hereby sincerely and solemnly declare that

1. I completed a doctoral course at Tsukuba University in March, 1985, being specialized in chemistry. Since April, 1985, I have been employed by Shin-Etsu Chemical Co., Ltd., assignee of the above-identified application, where I have been engaged in research and development of silicone material and silicone resin for electronic applications. I am one of the inventors of the above-identified application and I am familiar with the subject matter disclosed in the application as well as the disclosures in the references cited against the claims.

2. The relation between amounts of halogen and metallic impurities in coating compositions and properties such as dielectric constant, modulus and hardness of the films produced by the compositions were tested.

Examples 1 and 2, and Comparative Example 1 are described in the present specification. Comparative Example 2 was carried out using triethylmethylammonium hydroxide prepared in a different method as described below. Reference Examples 1 and 2 have additional steps of removing halogen and metallic impurities such as metal salts by washing with water to the steps of Examples 1 and 2, respectively.

Reference Example 1

The 16.5 g of an aqueous 26 wt% solution of tetramethylammonium hydroxide (made by Tokyo Kasei Company) was added to a mixture of 237 g of ultra-pure water and 471 g of ethanol and then uniformly stirred. The mixture of 44.9 g of methyltrimethoxysilane and 68.6 g of tetraethoxysilane was added dropwise thereto. The

resulting mixture was reacted at 60°C for two hours, then the pH thereof was adjusted to be 4.3 by adding an aqueous solution of maleic acid. Ethyl acetate was added thereto and washed with ultra-pure water five times. Propylene glycol monopropyl ether was added thereto, and concentrated at a reduced pressure until the siloxane concentration became 10 wt%. The resulting solution was then filtered with a filter made of Teflon™ having pore diameter of 0.05 _m, and consequently , coating composition (5) was obtained. The weight-average molecular weight of the product obtained by the hydrolysis and condensation of the alkoxysilane was about 150,000 as the result of measurement by GPC.

Comparative Example 2

Coating composition (4) was obtained in the same manner as in Example 2 except that 6.3 g of triethylmethylammonium hydroxide which had been produced by the reaction between triethylmethylammonium chloride (made by Tokyo Kasei Company) and potassium hydroxide was used in the place of triethylmethylammonium hydroxide which had been produced by the reaction between triethylamine and dimethyl carbonate. The weight-average molecular weight of the product obtained by the hydrolysis and condensation of the alkoxysilane was about 100,000 as the result of measurement by GPC.

Reference Example 2

The 6.3 g of triethylmethylammonium hydroxide which had been produced by the reaction between triethylmethylammonium chloride (made by Tokyo Kasei Company) and potassium hydroxide was added to a mixture of 237 g of ultra-pure water and 471 g of ethanol and then uniformly stirred. The mixture of 44.9 g of methyltrimethoxysilane and 68.6 g of tetraethoxysilane was added dropwise thereto. The resulting mixture was reacted at 60°C for two hours, then the pH thereof was adjusted to be 4.3 by adding an aqueous solution of maleic acid. Ethyl acetate was added thereto and washed with ultra-pure water five times. Propylene glycol monopropyl ether was added thereto, and concentrated at a reduced pressure until the siloxane concentration became 10 wt%. The resulting solution was then filtered with a filter made of Teflon™ having pore diameter of 0.05 _m, and consequently , coating composition (6) was obtained. The weight-average molecular weight of the product obtained by the hydrolysis and condensation of the alkoxysilane was about 160,000 as the result of measurement by GPC.

The contents of halogen and metallic impurities in the coating compositions obtained above are shown in Table 3, where the halogen impurity is based on chlorine by coulometric titration using the combustion method, and the metallic impurities were analyzed with ICP-MS.

The obtained coating compositions were spin-coated on a silicon substrate and sintered at 120°C for 2 minutes, 230°C for 3 minutes and 425°C for 60 minutes. Dielectric constant and mechanical strength of the obtained insulating films are shown in Table 4, where the dielectric constant was measured using the Mercury Probe Method and the modulus and hardness were measured using the nanoindentation method.

Table 3 Amounts of Impurities in Compositions.

	Coating composition	impurities (ppm)									
		halogen	Na	K	Fe	Ni	Cr	Ca	Al	Cu	Zn
Example 1	(1)	33	11	18	<5	<5	<5	<5	<5	<5	<5
Comp.Ex.1	(3)	21,300	630	56,000	<5	<5	<5	81	15	<5	<5
Ref.Ex.1	(5)	30	15	10	<5	<5	<5	<5	<5	<5	<5
Example 2	(2)	28	14	9	<5	<5	<5	<5	<5	<5	<5
Comp.Ex.2	(4)	35,200	415	54,500	28	<5	<5	33	21	<5	<5
Ref.Ex.2	(6)	32	14	12	<5	<5	<5	<5	<5	<5	<5

Table 4 Film properties

	dielectric constant	modulus (GPa)	hardness
Example 1	2.2	4.5	0.6
Comp.Ex.1	2.2	4.6	0.6
Ref.Ex.1	2.2	3.8	0.5
Example 2	2.0	3.2	0.4
Comp.Ex.2	2.0	3.3	0.4
Ref.Ex.2	2.0	2.8	0.3

3. Reduction of mechanical properties (espccially modulus) between Comparative Example 1 and Reference Example 1 and between Comparative Example 2 and Reference Example 2 shows that the presence of halogen and metallic impurities such as potassium increases the mechanical properties. On the other hand, the almost constant mechanical properties (especially modulus) between Comparative Example 1 and Example 1 and between Comparative Example 2 and Example 2 shows that the present invention can provide good mechanical properties keeping the halogen and metallic impurities low. Because the presence of halogen and metallic impurities is undesirable in the field of semiconductor, the present invention has a great advantage.

4. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize he validity of the application or any patent resulting therefrom.

Dated: July 18, '06